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Prediction of 1st and 2nd $E_{1/2}$ values for viologen-containing conjugated unimers and dimers from calculated pK_b values of the substituents.

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Abstract

A library of 18 conjugated, rod-like compounds with either one or two viologen residues have been synthesized and characterized electrochemically. Containing up to 8 aromatic/heterocyclic rings in conjugation, the members of the library differ in the substitution pattern of electron-withdrawing or -donating groups on the aromatic substituents of the viologen units. The first and second half-wave potentials of each member are found to be linearly correlated with the calculated pK_b values of the aromatic end-groups. This relationship will enable the half-wave potentials of related, novel, substituted viologen species to be predicted using a simple, empirical formula.

Introduction

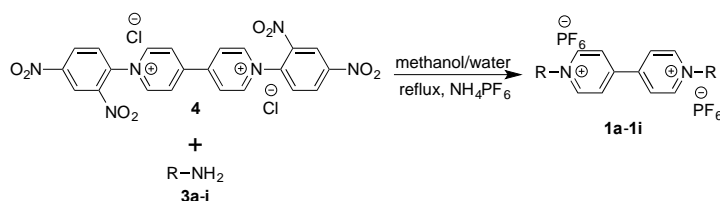
Viologens are disubstituted 4,4'-bipyridinium ions that can undergo two sequential one-electron transfer reactions to form firstly a radical cation and secondly a neutral quinoidal species.¹ The electron-deficient nature and reversible redox properties of substituted viologens has seen them become ubiquitous entities in a wide range of research fields including supramolecular chemistry,² electrochromic displays,³ photovoltaic cells,⁴ sensors,⁵ electron-transfer photosensitizers⁶ and catalytic hydrogen generation.⁷ They are also emerging as key components of functional MOFs including those used for carbon sequestering.⁸ Very recently, synthetic and analytical studies of conjugated rod-like viologen containing compounds by our group⁹ and by Zhao *et al.*¹⁰ have shown them to exhibit unique redox properties and self-assembly characteristics.

The reversible redox properties of the viologen are generally key to the functionality of the system, and so knowledge of the precise half-wave potential ($E_{1/2}$) of the viologen is of vital importance. Within the extensive number of viologen species reported to date, there has been some attempt to investigate how the structure of the *N*-substituent affects the redox properties of the viologen.¹¹ However, it is clear that $E_{1/2}$ is also dependent on the solvent, counterion and counter-electrode.¹² The non-uniformity of conditions used during electrochemical analysis by different research groups thus hinders direct comparison of data from these sources. Indeed, until the present work, there has been no systematic structure/property investigation of aromatic *N,N'*-substituted viologens under directly comparable conditions.

Herein, we use the optimized Zincke-type¹³ reaction conditions reported previously^{9, 14} in a modular synthesis to produce a library of 18 π -conjugated unimers (**1a-i**) and dimers (**2a-i**) containing either one or two viologen residues respectively. The members of each series differ in the substitution patterns on the non-viologen, aromatic rings. The redox properties of the members of this series are compared so as to correlate the effect of the structure of the substituents on the half-wave reduction ($E_{1/2}$) potentials of the viologen residue.

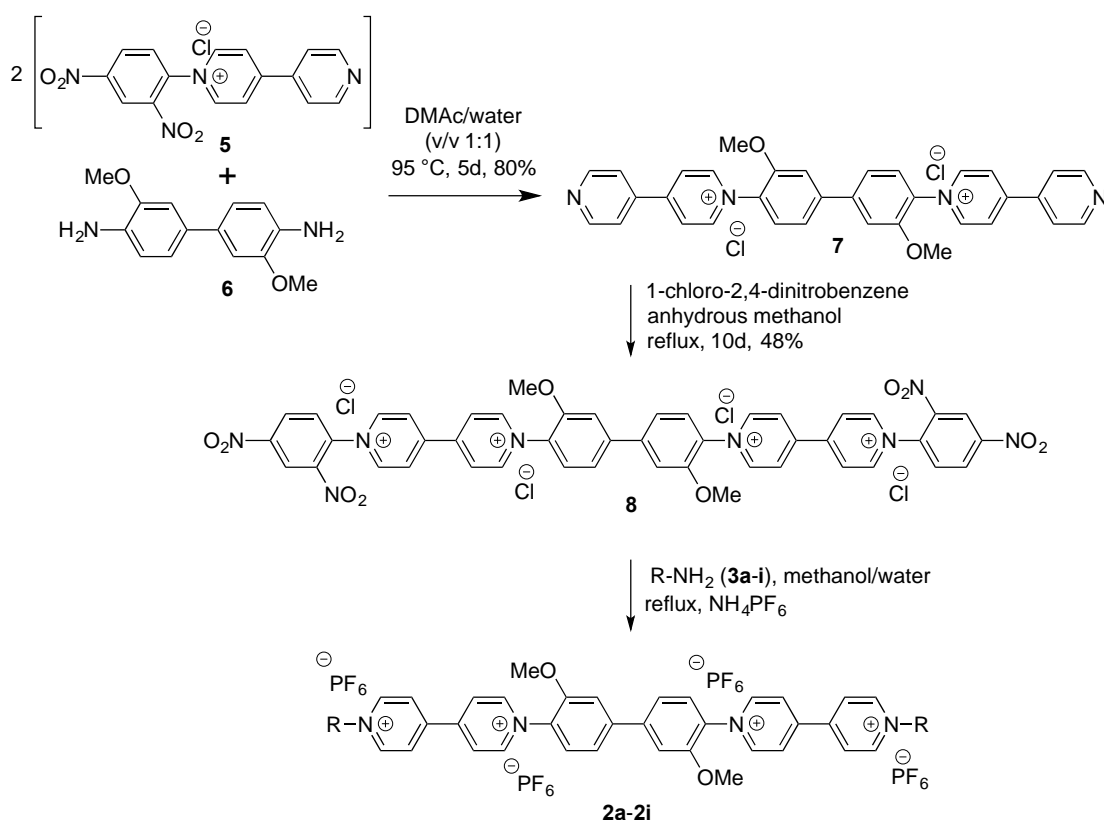
Results and discussion

The synthesis of aryl-substituted viologen unimers was achieved by reaction of the appropriate aryl amine (**3a-i**, for structures see table 1) with the well-known di-Zincke salt **4**.^{14,15} The aromatic end groups were selected to fall into one of three structural types, having either electron withdrawing substituents (**3a**, **3b**) or electron donating substituents (**3c-3f**), or else containing varying numbers of fused aromatic rings (**3g-3i**). During the synthesis of the unimers, each double substitution reaction proceeded cleanly under identical conditions to give the target compounds in high and reproducible yields (>80%).¹⁶



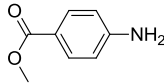
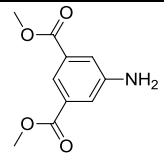
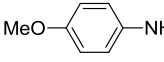
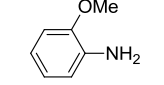
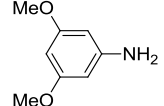
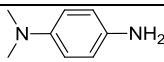
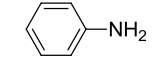
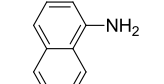
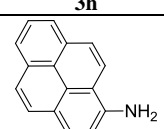
Scheme 1 Synthesis of mono-viologen species **1a-h**. For the structures of amines **3a-i** see Table 1.

Synthesis of the dimeric series of compounds started with double addition of Zincke salt **5**¹⁷ to 3,3'-dimethoxybenzidine (**6**), which we have shown previously to be a good partner in the Zincke reaction.⁹ Addition of 1-chloro-2,4-dinitrobenzene to intermediate **7** resulted in the formation of di-Zincke salt **8** which was the common intermediate for the synthesis of the series of di-viologen conjugated systems **2a-h**. As can be seen from Table 1, the target di-viologen compounds (**2a-2i**) were mostly isolated in good yields, although **2c** and **2f** could not be isolated cleanly under these general reaction conditions.



Scheme 1 Syntheses of bis-viologen species **1a-h**. For the structures of amines **3a-i** see Table 1.

Table 1: Yields, calculated pK_b values and $E_{1/2}$ values for the unimeric and dimeric viologens synthesized in this work

Aromatic mono-amine	Unimeric viologen series				Dimeric viologen series			
	Compound (Yield)	Calc. ^a pK_b	$E_{1/2}$ (V) ^b		Compound (Yield)	Mean Calc. ^c pK_b	$E_{1/2}$ (V) ^b	
			1st	2nd			1st	2nd
 3a	1a ¹⁸ (93%)	2.7	-0.583	-0.794	2a (95%)	3.55	-0.619	-0.900
 3b	1b ⁹ (93%)	1.3	-0.609	-0.830	2b ⁹ (77%)	2.85	-0.629	-0.921
 3c	1c ¹⁹ (95%)	5.1	-0.705	-1.026	2c (n.d.)			
 3d	1d (92%)	4.4	-0.689	-1.041	2d (85%)	4.4	-0.669	-1.046
 3e	1e (79%)	3.5	-0.654	-0.931	2e (90%)	3.95	-0.660	-0.976
 3f	1f (81%)	6.1	-0.770	-1.107	2f (n.d.)			
 3g	1g ²⁰ (96%)	4.6	-0.664	-0.946	2g (87%)	4.5	-0.679	-0.996
 3h	1h ¹⁹ (87%)	4.1	-0.664	-0.991	2h (92%)	4.25	-0.664	-1.007
 3i	1i (85%)	4	-0.664	-0.981	2i (95%)	4.2	-0.659	-0.996

a) Calculated using software that can be access from reference²¹; b) solutions in anhydrous DMF at a glassy carbon disc electrode (d = 2 mm) at $v = 500 \text{ mV s}^{-1}$. For voltammograms see the SD; c) average pK_b for the amine on the midblock **5** (calculated²¹ $pK_b = 4.3$) and the appropriate mono-amine (**3a-i**)

As expected, all these viologen species exhibit two distinct reversible redox couples (for detailed cyclic voltammetry (CV) and square wave voltammetry (SWV) data see SD). However, the precise value of each half-wave potential is highly dependent on the nature of the aromatic end group. For example, compound **1a** containing an electron-

withdrawing ester substituent ($1^{\text{st}} E_{1/2} = -0.583$, $2^{\text{nd}} E_{1/2} = -0.794$) undergoes each reduction process at a lower potential than compound **1f** which contains two electron donating dimethyl amino residues ($1^{\text{st}} E_{1/2} = -0.770$, $2^{\text{nd}} E_{1/2} = -1.107$).

To allow for a more quantitative analysis of the effects that the aromatic substituents have on the electronic structure of the viologen, pK_b values for **3a-i** were determined using the *ACE and JChem acidity and basicity calculator*²¹ (For values see Table 1). This tool has been validated and used by many researchers to estimate the pK_a and pK_b values of a diverse range of molecules.²²

Plots of the first and second $E_{1/2}$ as a function of pK_b for each unimeric viologen species both exhibit linear relationships ($R^2 \geq 0.8$) over the range studied (Figure 1). The negative slope of each plot confirms that the more electron-donating the amine endgroups, the more energy is required to reduce the associated viologen residue.

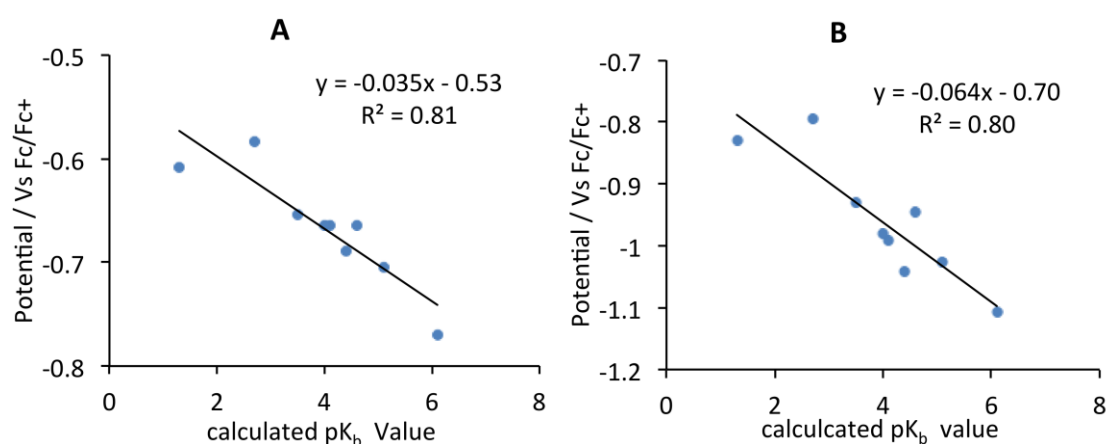


Figure 1: Plots of $1^{\text{st}} E_{1/2}$ (A) and $2^{\text{nd}} E_{1/2}$ (B) as a function of the calculated pK_b of the aromatic amine endgroups for unimeric viologen species **1a-i**.

Although there is a smaller variation in $E_{1/2}$ across the series of dimers (**2a-i**) compared to the unimeric series, we also investigated the relationship between pK_b and $E_{1/2}$ values in these more complex molecules. Inspection of the dimeric structure (Scheme 2) shows that the viologens in each dimer are each connected to the midblock (**5**) through one pyridinium nitrogen and to the end group through the outermost pyridinium group. It was therefore decided to average the pK_b for the amine on the midblock **5** (calculated $pK_b = 4.3$) and for the amine on the end group, to provide an estimate for the combined electron donating ability of the substituents at either end of the viologen. As can be seen from Figure 2, plots of both first and second $E_{1/2}$ as a function of mean pK_b for each

dimeric viologen species do indeed exhibit an approximately linear relationship ($R^2 \geq 0.7$) over the range studied. This result demonstrates that calculated pK_b values can be used to provide good estimates of both the 1st and 2nd reduction potentials of large rod-like species containing multiple viologen residues that have different aromatic substituents at the *N*-termini.

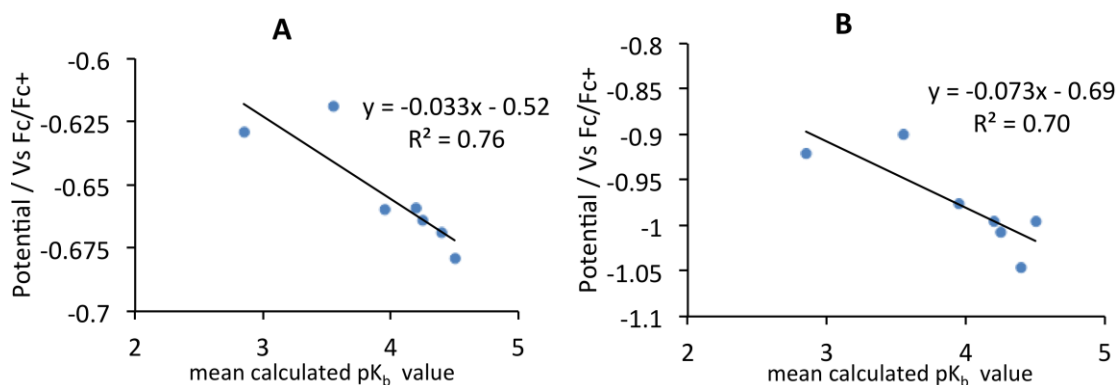


Figure 2 Plots of 1st $E_{1/2}$ (A) and 2nd $E_{1/2}$ (B) as a function of the calculated mean pK_b of the aromatic substituents for dimeric viologen species **2a-i**.

Conclusions

In this paper, a series of 18 rod-like, conjugated systems containing either one or two viologen residues and a range of aromatic end groups with different substitution patterns have been synthesised and their electrochemical properties investigated. All the compounds undergo reversible stepwise two-electron reduction of each viologen moiety. Comparison of all of the unimers and dimers shows a strong correlation between the half-wave potentials and pK_b values of the amine residues of the end groups: higher end group pK_b values increase the energy required to reduce the viologen species. The identification of this correlation over a broad range of aromatic end groups will allow the $E_{1/2}$ values of viologen species to be finely tuned to optimise this property for a multitude of applications.

Acknowledgement

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Supplementary Data

Supplementary data (SD) including full experimental procedures and characterization data, ¹H NMR spectra and voltammograms can be found at:

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